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(54) A CONTINUOUS PRODUCTION OF IRON OXIDE BLACK PIGMENTS

- (71) We, BAYER AKTIEN-GESELLSCHAFT a body corporate organised under the laws of the Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to the continuous production from oxide black pigments. Iron oxide black pigments of the chemical composition Fe_3O_4 have a magnetite structure with a cubic habit. They are precipitated from solutions of iron salts, usually sulphates obtained in the form of the heptahydrate, for example as by-product from pickling plants. The precipitating agents used are alkali metal solutions, usually sodium hydroxide or sodium carbonate solutions, and the precipitates obtained are oxidized in an alkaline medium at pH values of from 7 to 14 at elevated temperatures of from 50 to 100°C. This oxidation is preferably carried out in gasification reactors using atmospheric oxygen.
- Preparation of iron oxide black pigments is generally carried out in batches but processes have become known which deal with the continuous production of magnetite. Thus, for example in Ind. Eng. Chem. 44 (1952), page 676, a process is described in which pickling liquors containing iron sulphate are used as starting materials. The liquors are treated with sodium hydroxide solution at a pH of up to 13.5 in a stirrer vessel and oxidation to form the pigment at an elevated pressure and at a temperature of 160°C. Carrying out this process on a commercial scale presents difficulties on account of the necessity for continuous removal of solids from the autoclaves.
- The fundamental difference between the continuous and batch process is that in the batch process the reaction times of the starting materials can be accurately controlled. On the contrary, in the continuous process, there is a risk that parts of the solutions or suspensions will be prematurely discharged from the reaction while other parts are liable to be left too long under the reaction conditions. One consequence of this is that the particles of pigment obtained are not uniform in size. In pigments, it is important to keep to a narrow range of particle sizes because this is a means of obtaining a purer colour tone and higher colour density.
- It is known that the residue time in stirrer vessels can be restricted to a narrow range by connecting several such vessels in series to form a cascade. If, in such a cascade, the material is arranged to pass through the containers from below in an upwardly direction, it is virtually impossible for individual particles to pass through the apparatus along the shortest path and not be caught by the suction of the stirrers. A process which is based on the principle of reactors connected in series is described in British Patent Specification No. 1,255,620. In this process, the preparation of iron oxide black pigment from iron chloride solution and ammonium hydroxide or sodium hydroxide using sodium nitrate as oxidizing agent is carried out in a horizontal segmented reactor equipped with a plurality of stirrer discs.
- The disadvantage of the use of this reactor is that it necessitates the use of an oxidizing agent other than air.
- It is an object of the present invention to prepare iron oxide pigments of intense colour and narrow range of particle sizes by a continuous process in a cascade of stirrer vessels, using air as the oxidizing agent. It is found that operation in a plurality of gasification vessels connected in series is not sufficient to achieve this object.
- It is necessary to observe additional conditions which are all aimed at producing a more rapid oxidizing reaction. It has been found that the oxidation time required for the formation of Fe_3O_4 depends on the

temperature, the pH and the iron oxide concentration in the magnetised suspension discharged from the last gasification vessel. This oxidation time is surprisingly found to increase with decreasing iron oxide concentration in the discharging suspension.

Accordingly, the present invention provides a process for the continuous preparation of iron oxide black pigments of magnetite structure wherein a ferrous salt solution and a solution of a basic precipitating agent are introduced into the first vessel of a cascade of vessels, wherein the resulting suspension is oxidised to Fe_3O_4 by bubbling through a free oxygen-containing gas, preferably air, the oxidation being carried out simultaneously in each vessel of the cascade at a pH value of from 9 to 10 and a temperature of 60 to 80°C, preferably 70 to 80°C, while the iron oxide concentration in the suspension discharged from the last vessel is 30 to 50 g of Fe_3O_4 per litre, and wherein the resulting black oxide pigment is recovered.

Very short reaction times of 40 to 60 minutes are obtained under the conditions according to the invention. The process according to the invention is preferably carried out in a cascade of stirrer vessels. It is particularly advantageous to carry out oxidation in three stages, i.e. in three vessels. Deviations in the upward or downward direction from the parameters which are to be observed according to the invention result in a considerable increase in the reaction times to values of up to 3.5 hours and the pigment obtained has a correspondingly wider distribution of particle sizes and weaker colour. The pH of from 9 to 10 which according to the invention must be observed in each individual stage of the process is measured with a glass electrode measuring chain.

The concentration of iron oxide in the discharging suspension can be adjusted either by altering the concentration of starting solutions or by adding water in one of the three stages, mainly in the first stage of the process. The starting material used in the process according to the invention is preferably iron sulphate but other iron salts such as ferrous chloride or commercial products such as iron sulphates from steel pickling plants or iron sulphates obtained as waste products of the production of TiO_2 pigments from ilmenite may also be used without requiring a special preliminary step for separation of the impurities. The basic precipitating agent used is preferably NaOH or ammoniacal water. The basic precipitating agents are preferably used in the form of aqueous solutions at a concentration of 10 to 30% by weight whereas the iron salt solutions are

preferably adjusted to concentrations of 5 to 20% by weight. The oxygen-containing gas used for oxidation of the ferrous ions may be air or air enriched with oxygen. In the latter case, a further increase in the reaction velocity can be achieved.

The oxygen-containing gases may be supplied by known methods, either using gasification stirrers of the kind used in the treatment of effluent or in fermentation work, or using high speed stirrers such as turbine impellers, for example, and supplying the air from below, either at separate points or from a gasification ring. Other gasification systems capable of distributing the oxidizing agent in the form of fine bubbles are also suitable. Oxidation of the ferrous ions is preferably continued until the ratio of $\text{Fe}^{(III)}$ to $\text{Fe}^{(II)}$ in the suspension discharged from the last gasification vessel is 1.8.

In that case, the ratio can be increased to 2 by reoxidation when the product is subsequently dried.

It has been found that when the individual gasification vessels are equal in size, the ratio by weight of $\text{Fe}^{(III)}$ to $\text{Fe}^{(II)}$ in the second and third vessel is about twice that in the preceding vessel.

The pH-values measured as indicated above drop slightly from each vessel to the next so that the overall difference between the pH in the first vessel and in the last is about 0.5.

The pigments obtained according to the invention have an average particle size of 0.1 to 0.2 μm and a spectrum of 0.05 to 0.3 μm . Their use lies mainly in the pigmentation of lacquers, synthetic resins and concrete parts.

The process according to the invention will now be illustrated in more detail with the aid of Examples.

Example 1

An iron sulphate solution containing 104 g of FeSO_4 per litre and sodium hydroxide solution containing 189 g of NaOH per litre were continuously introduced into the first gasification vessel through inlet pipes at the bottom. The mixture of the two solutions flowed through three vessels of equal size, in each case from below in an upwardly direction and air was passed through the vessels at the same time. The air was distributed in the vessels from ring nozzles at the bottom at the rate of 200% by weight of the stoichiometric quantity. Disc stirrers were installed to ensure good contact between gas, solid and liquid. The stirrers rotated at a circumferential velocity amounting to 5 metres per second on the outermost circumference of the disc. The temperature in the vessels was adjusted to 70°C by external heating.

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The air escaping from the system was recoiled and the condensate was returned to prevent loss of steam as far as possible. The pH was 9.7 in the first vessel and settled at 9.4 in the second and 9.2 in the third. The ratio of $\text{Fe}^{(III)}$ to $\text{Fe}^{(II)}$ was 0.5 in the first vessel, 1.0 in the second and 1.85 in the third. The concentration of pigment in the discharge from the third vessel was 41.8 g of Fe_3O_4 per litre. The volume/time yield was 53.7 g Fe_3O_4 per litre per hour. This means that the average time of stay in the three gasification vessels was 47 minutes.

The pigment obtained after filtration, washing and drying at 70°C in a circulating air oven or spray drier had a specific surface area of $9.8 \text{ m}^2/\text{g}$, an average particle diameter of $0.13 \mu\text{m}$ and a distribution range of from 0.05 to $3.0 \mu\text{m}$. It has double the colour intensity of a comparison pigment obtained according to Example 5.

Example 2 (Comparative)

An iron sulphate solution containing 208 g of FeSO_4 per litre and a sodium hydroxide solution containing 378 g of NaOH per litre were used in the same plant as in Example 1. An iron oxide suspension containing 75.3 g of Fe_3O_4 per litre was obtained at the same temperature and pH. To ensure adequate oxidation, it was necessary to increase the time of stay to 1 hour 45 minutes by reducing the rate of feed of material. The volume/time yield therefore drops to 43.3 g of Fe_3O_4 per litre per hour. The average particle size of the pigment obtained was $0.2 \mu\text{m}$ and the distribution range between 0.05 and $0.5 \mu\text{m}$. The specific surface area was $8.0 \text{ m}^2/\text{g}$ and the colour intensity was in the region of 20% lower than that of the pigment from Example 1.

Example 3 (Comparative)

The process was carried out at pH 7, using the same concentration of starting materials and temperature as in Example 2. The even longer oxidation time required for obtaining the desired $\text{Fe}^{(III)}/\text{Fe}^{(II)}$ ratio of 1.8, which was in this case 1 hour 50 minutes, caused a further concentration of the solution due to slight loss of steam.

The Fe_3O_4 content in the discharging suspension was 77.2 g/l. The volume/time yield was 41.8 g of Fe_3O_4 /h. The specific surface area was reduced to $7.5 \text{ m}^2/\text{g}$. The average particle size was $0.22 \mu\text{m}$ and the distribution range from 0.05 to $0.5 \mu\text{m}$. The colour intensity of the pigment was about 25% lower than that of the pigment from Example 1.

Example 4 (Comparative)

Instead of employing a pH of 7 as in Example 3, this process was carried out at

pH 11 by using an excess of NaOH . The conditions were otherwise the same as in Example 3; Reaction temperature 70°C and starting concentrations of 208 g of FeSO_4 /l and 378 g of NaOH /l. The pigment concentration in the third vessel rose to 81.4 g of Fe_3O_4 per litre and the reaction time increased to 2 hours and 30 minutes. The volume/time yield was in this case only 32.9 g of Fe_3O_4 /h. The specific surface area was $6.0 \text{ m}^2/\text{g}$ and the colour intensity was about 33% lower than that of the pigment from the Example 1.

Example 5 (Comparative)

The operating conditions were the same as in Example 4 except that the reaction temperature was raised to 90°C . The oxidation time was increased to 3 hours 35 minutes. A pigment concentration of 85.4 g of Fe_3O_4 per litre was obtained before the stage of filtration, which corresponded to a volume/time yield of 23.9 g of Fe_3O_4 /h. The specific surface area of $5.3 \text{ m}^2/\text{g}$ showed that the pigment was more coarsely grained. This was also evident from the average particle size of $0.3 \mu\text{m}$ and distribution range of from 0.1 to $0.7 \mu\text{m}$. The pigment had only half of the colour intensity of the pigment obtained in Example 1.

WHAT WE CLAIM IS:—

1. A process for the continuous preparation of an iron oxide black pigment having a magnetite structure wherein a ferrous salt solution and a solution of an alkaline precipitating agent are introduced into the first vessel of a cascade of vessels, wherein the resulting suspension is oxidized to Fe_3O_4 by bubbling through a free oxygen-containing gas, the oxidation being carried out simultaneously in each vessel of the cascade at a pH value of from 9 to 10 and at a temperature of 60°C to 80°C while the concentration of iron oxide in the suspension discharged from the last vessel is maintained at 30 to 50 g of Fe_3O_4 /l and wherein the resulting iron oxide black pigment is recovered.

2. A process according to claim 1, wherein oxidation is carried out in three separate vessels.

3. A process according to claim 1 or 2, wherein the free oxygen-containing gas is air.

4. A process according to any of claims 1 to 3, wherein ferrous salt is ferrous sulphate.

5. A process according to any of claims 1 to 4, wherein the ferrous salt solution has a concentration of from 5 to 20% by weight.

6. A process according to any of claims 1 to 5, wherein the alkaline precipitating

- agent is an aqueous solution having a concentration of from 10 to 30% by weight.
7. A process according to any of claims 1 to 6, wherein oxidation of ferrous ions is continued until the ratio of $\text{Fe}^{(III)}$ to $\text{Fe}^{(II)}$ in the suspension discharged from the last vessel is 1.8.
8. A process according to any of claims 1 to 7, wherein the resulting iron oxide black pigment is filtered off, washed and dried.
9. A process for the continuous preparation of an iron oxide black pigment substantially as herein described with reference to Example 1.
10. An iron oxide black pigment when prepared by a process according to any of claims 1 to 9.

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